EMERGING CONTAMINANTS

What are they?

Pharmaceuticals, including antibiotics and birth control pills, and personal care products are one group of emerging contaminants. *Photo: US Department of Defense*

An emerging contaminant is a substance for which there is increasing evidence of environmental occurrence and that the substance may cause adverse human and/or environmental health effects. The term is shorthand for "contaminants of emerging concern". There are two general reasons why concern about a substance can be emerging. The first is technological improvements: some emerging contaminants may have been present in the environment for a long time but new measurement methods improve our ability to detect them. The second reason is emergence of a compound not previously common in the environment due to a new substance being manufactured, or recent changes in use or disposal practices of existing substances. Research on the occurrence and health effects of these contaminants is important to characterize the nature of the risk and decide what actions may be required to protect human and environmental health.

Emerging contaminants consist of a range of substances, many of which are produced synthetically, and may enter the environment in wastewater from municipal or industrial sources. Treatment of municipal wastewater typically lowers the concentrations of emerging contaminants, but considerable levels may remain after treatment. Groundwater is impacted if contaminants in treated wastewater infiltrate to groundwater. Emerging contaminants may also enter the environment from agricultural wastes, which may be solid or liquid. Agricultural wastes are often land-spread to make nutrients from the wastes available to crops, but if the wastes contain contaminants, they may migrate toward groundwater as irrigation water, rainwater or snowmelt infiltrate.

Degradation processes, if they occur, can reduce the amount of contaminant that makes it to groundwater. Degradation can be abiotic--for example, through reaction with water, known as hydrolysis—or biotic, meaning that a microbial organism starts a chemical reaction, in which the organism uses some of the original molecule but the rest—a *metabolite*—is left over. Degradation is normally only considered to be complete if all of the parent compound is converted to other naturally occurring chemicals, such as carbon dioxide (CO_2), water (H_2O), and dinitrogen gas (N_2). Incomplete degradation, also known as transformation, is when the parent compound transforms into one or more metabolites but not all the way to naturally occurring chemicals.

Another process that can reduce the amount of a contaminant that arrives in groundwater is *sorption*. Sorption is a physical/chemical reaction in which substances, dissolved or suspended in water, form a bond with minerals or soil organic matter, attaching them to the solid material. Sorption can be reversible, meaning that *desorption* can also occur later. Desorption can occur when the concentration of the same substance in infiltrating water decreases. This can happen, for example, during a large rain event. If a contaminant desorbs under commonly occurring conditions, sorption only increases the amount of time before contaminants make it to groundwater.

Emerging contaminants for which a laboratory analytical standard (i.e., the pure substance dissolved in water or another liquid at a known concentration) exists are often measured with *liquid chromatography with mass spectrometry detection* (LCMS). With this technique, a liquid sample is injected into the laboratory instrument, with or without procedures to "clean up" the sample by removing other compounds that may interfere with measurement. Substances within the sample are then ionized with an electrical charge, and ionized portions of the substances are detected with *mass spectrometry*. The results of mass spectrometry can then be used to determine the molecular weight of the substances in the sample under investigation and identification of specific compounds in the sample can be made.

Technologically advanced variations of this technique include the use of *tandem mass spectrometry detection* (MS/MS), in which two different methods of ionizing the chemicals dissolved in water are used, creating more fragments of the original substance. MS/MS is used for the measurement of Per- and Polyfluorinated Alkyl Substances (PFAS), an important group of emerging contaminants.

Availability of a laboratory analytical standard of a substance is necessary for definitive detection and quantitation. However, emerging research laboratory techniques use high resolution mass spectrometry (HRMS) to obtain a more holistic picture of the variety of chemical compounds present in a sample, including ones for which an analytical standard does not exist. When emerging contaminants are known or suspected to transform, HRMS is particularly useful for finding the metabolites. HRMS is also useful for detecting compounds in the second category of emerging contaminants—newly manufactured substances—for which a laboratory analytical standard may not yet exist. The information on the combinations of split fragments can be compared to a library of possible molecules. From this comparison, inferences about possible chemicals (including metabolites) present can be made, even without a laboratory analytical standard for the substance. HRMS laboratory devices are more expensive and currently less commonly available than LCMS (including ones with MS/MS capability).

The following sections give information on categories of emerging contaminants that may be found in Wisconsin groundwater.

Pharmaceuticals and Personal Care Products

Pharmaceuticals enter the environment through disposal of unused pills as well as excretion of the compounds or their metabolites from the human body. A metabolite is a compound produced by the body's metabolism from the "parent" compound, i.e. the original pharmaceutical. Metabolites often, but not always, have similar chemical properties as the parent compound. Pharmaceuticals detected in groundwater worldwide include antibiotics, non-steroidal anti-inflammatory drugs, birth control medications, and many other prescription medicines. Many pharmaceuticals begin to degrade in soil passage or groundwater, but the presence and types of metabolites are, to a large extent, still being discovered. Stimulants such as caffeine and nicotine, as well as recreational drugs, may also be found in groundwater.

Together, pharmaceuticals and personal care products (PPCPs) - including shampoos, detergents and "over-the-counter" non-prescription medicines - make up a category of emerging contaminants that largely enter the environment from domestic wastewater and municipal sources. Point sources of PPCP discharge into the environment include wastewater treatment plants, which may remove some but not all of these compounds from wastewater, discharge from septic systems, land application of wastewater septage and leakage from older landfills.

Per- and Polyfluorinated Alkyl Substances (PFAS)

A group of emerging contaminants of much current concern are perfluoroalkyl and polyfluoroalkyl substances (PFAS). These molecules are comprised of organic carbon chains in which some (poly-) or all (per-) hydrogen atoms have been replaced with fluorine atoms. PFAS have been used in a variety of industry and consumer products since the 1940s and are now being detected in groundwater and drinking water supplies worldwide. PFAS gained widespread use in part due to their ability to repel water and oil and withstand high temperatures. They are found in numerous consumer products, such as non-stick cookware, stain- and water-repellent clothing and carpeting, grease-resistant liners to food packaging including microwave popcorn, some spray paints, and Class B fire-fighting foams (fires involving flammable liquids).

Many polyfluorinated substances that are part of the PFAS chemicals family transform in the environment to other PFAS, especially to perfluoroalkyl acids such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS). However, PFAS are not known to degrade in groundwater or elsewhere in the environment into any non-toxic end products. Therefore, they may accumulate in environmental settings. Ways PFAS can enter the environment include placement of PFAS-containing products in landfills, use of the products in combination with water resulting in their presence in wastewater, spreading of biosolids (a product of wastewater treatment) on cropland to replenish soil organic matter, and direct use and lack of containment of the chemicals at manufacturing and firefighting sites.

The two most widely studied PFAS are PFOA and PFOS, both of which present health risks and are commonly found in groundwater. While these two substances may have been manufactured directly during the mid-20th century, manufacturing shifted during the late 20th century to polyfluorinated substances (precursors) that may transform to end products, including but not limited to PFOA and PFOS. These compounds may transform slowly in soil and groundwater, representing ongoing sources of PFOA and PFOS to the environment. Since the turn of the century, manufacturing has shifted to shorter chained compounds such as perfluorobutane sulfonate (PFBS) and its precursors, in applications where previously PFOS or its precursors was used. Additionally, manufacture of PFAS containing additional chemical structures (e.g. ethers) has emerged, with this category of PFAS being known as "replacements". Examples of replacement PFAS are hexafluoropropylene oxide dimer acid (HFPO-DA, sometimes referred to by the trade name "GenX", (a replacement of PFOA) and PFBS (a replacement of PFOS). PFBS and HFPO-DA are among the compounds that were evaluated by the Wisconsin Department of Health Services and that agency has provided recommendations for groundwater quality standards for the two substances to the DNR.

For more information on PFAS, please see the PFAS section of the report.

Pesticides and other Agricultural Contaminants

In many agricultural practices, pesticides are applied to crops to kill or hinder the effects of "pests", which can be insects, competing plants (weeds), fungi, and bacteria. On large areas of crops, application is done from small airplanes to distribute the chemicals over a large area. Due to crop irrigation and precipitation events, pesticides may leach into groundwater. Although about 30 pesticides are currently regulated in Wisconsin, over 90 are known to be used.

Most pesticides can sorb to soil and aquifer material, meaning they often travel to and through groundwater more slowly than the water itself. Some are also transformed into metabolites by bacteria. Active methods of destroying pesticides include photocatalytic techniques, which combine use of light and chemicals to "catalyze" pesticide-destruction reactions.

Although pesticides have been in use since the middle of the 20th century, new pesticides continue to come into use. One such pesticide is the herbicide isoxaflutole, which currently has approval for limited use for weed control on corn crops. Field testing, to evaluate potential groundwater impacts from Isoxaflutole use, are currently underway. For more information on pesticides, please see the pesticides section of the report.

Though functionally part of the PPCPs category of emerging contaminants, antibiotics and anti-parasitical drugs are also used in agriculture, to prevent infection outbreaks in mass raising of livestock. The overall amount of antibiotics used in such applications may be similar to or even greater than usage of antibiotics in human medicine, but generally fewer antibiotic substances are used in livestock applications. An example of a livestock antibiotic is sulfamethazine. Sulfamethazine has a tendency to sorb to soil and can be transformed under toxic conditions, but it may not be fully degraded to naturally occurring chemicals. Another type of contaminant from agriculture is hormones. Steroid hormones have been found in a study of dairy wastewater (Zheng et al., 2008).

Microbial Contaminants

Microbial contaminants such as viruses and pathogenic bacteria can be contaminants in groundwater. In fact, most bacteria that exist in the natural environment are thought to present little if any human health risk. Some bacteria can also improve water quality by degrading other emerging contaminants (e.g. PPCPs). However, a few bacteria are pathogenic (disease causing) and can cause human health impacts. Areas where soil is thin and groundwater supplies are drawn from a carbonate (limestone/dolomite) bedrock aquifer may be especially susceptible to microbial contamination.

Two sources of microbial contaminants are manure from livestock and human sanitary sewage. Pathogenic microbes from these sources may cause gastrointestinal illnesses, sometimes severe. A common type of enteric bacteria (bacteria that reside in the gut of humans and other animals) is *Escherichia coli* (commonly referred to as *E. coli*). Most *E. coli* strains are harmless, but pathogenic strains exist, for example the Shiga toxin-producing strain *E. coli* O157:H7. Water tests for *E. coli* detect a strain of *E. coli* that itself is harmless, but which is a good indicator that pathogenic microbes may be present.

Viruses in groundwater include norovirus, adenovirus and enterovirus. Viruses generally cannot reproduce without a host, but they can infect bacteria. A virus that infects, or replicates within bacteria is referred to as a "bacteriophage" (or simply "phage"). This usage of bacteria as hosts may enable viruses to survive longer in groundwater.

Antibiotic resistance is considered by the World Health Organization to be a major threat to health, food security, and development. After usage of an antibiotic, there is a tendency for bacteria that survived previous applications of the substance to become a larger part of the overall bacterial population—this phenomenon is antibiotic resistance. While antibiotics are used in both human and veterinary medicine, a greater number of antibiotic compounds are thought to be used in humans. As a consequence of antibiotic use in human medicine, multi-resistant bacteria (i.e., bacteria resistant to more than one antibiotic) have been found in clinical settings. Antibiotic resistance has been found in municipal wastewater discharge in studies in Europe, with patterns indicating that the resistance developed in clinical settings is spreading into the environment (Pärnänen et al. 2019). In another study, a strain of *E. coli* resistant to multiple antibiotics was found in hospital wastewater, although community wastewater appeared to be a greater overall contributor of antibiotic resistance (Paulshus et al. 2019). In a study of groundwater impacted by dairies in California (Li et al. 2014), antibiotic resistant *E. coli* bacteria were found in one sample, indicating potential for antibiotic resistant bacteria to be present in groundwater.

For more information on microbial pathogen, see the Pathogens section of the report.

Microplastics

Microplastics are small pieces of plastic, often less than 1 millimeter in size. The name "micro" broadly refers to the size range of micrometers—a micrometer is one one-thousandth of a millimeter. Some microplastics are produced at this size for specific (industrial) purposes, while others are breakdown products of larger plastics (SAPEA, 2019). Microplastics have been found in marine environments for decades (Rochman, 2018), but more recently are being discovered in terrestrial environments, including Lake Michigan (Mason et al., 2016). A recent study published in the journal *Science* found atmospheric deposition of on average 132 plastics per square meter every day on western U.S. protected lands (Brahney et al., 2020). Microplastics appear to accumulate in soils, including ones used for agriculture (Rochman, 2018). A recent study found microplastics—possibly leaked from septic systems—in karst groundwater in Illinois (Panno et al., 2019). While infiltration of water through soils might slow, minimize, or prevent the spread of microplastics into groundwater due to the filtering effect of soils, karst groundwater is particularly susceptible to contamination because water often is present in open fractures. While Wisconsin also has near-surface karst groundwater in some parts of the state, no studies of microplastics in the State's groundwaters are known.

Other Emerging Contaminants

Emerging contaminants not discussed above but which have been studied worldwide include flame retardants, phthalates and other plasticizers, and nanomaterials. Flame retardants are substances that are added to household, commercial building or other products to reduce flammability. A subset of flame retardants of particular concern are brominated compounds, such as polybrominated diphenyl ethers (often abbreviated "PBDEs") and polybrominated biphenyls (often abbreviated "PBBs").

Phthalates are used in bendable plastics as softening agents but are not chemically bound to the plastic and can leach out into water. Research indicates that they might not bioaccumulate (unlike many other synthetic organic compounds), but they have been found to be endocrine disrupting compounds, or substances that disrupt endocrine systems of humans and animals.

Nanomaterials are industrially produced physical particles that are between approximately 1 and 100 nanometers in size (there are one million nanometers in one millimeter). They have diverse uses in industry and commercial products, such as electronic components, paints and coatings, ultraviolet blockers in sunscreens, telecommunication, packaging materials and auto parts.

Occurrence in Wisconsin

The occurrence of emerging contaminants in Wisconsin is not easily generalized, but several studies supported by the GCC have investigated the potential for certain emerging contaminants to enter groundwater from specific sources.

PFAS.

For information on the occurrence of PFAS in Wisconsin's groundwater, please see the PFAS section.

Pharmaceuticals and Personal Care Products.

Antibiotics have been detected in treated wastewater effluent from facilities across the state, with very low concentrations of tetracycline and sulfamethoxazole detected in groundwater directly adjacent to a wastewater treatment facility groundwater discharge site (Karthikeyan and Bleam, 2003). Acetaminophen (Tylenol), paraxanthine (a caffeine metabolite) and the hormones estrone and β-estradiol have been detected in private on-site wastewater treatment system (POWTS) effluent in a Dane County study (Bradbury and Bahr, 2005), and estrogenic endocrine disrupting compounds (EDCs) were detected in POWTS effluent in a southeast Wisconsin study (Sonzogni et al., 2006). Neither study detected these compounds in groundwater. A follow up study at the Dane County site, ten years after subdivision development, however, found a number of contaminants that may have moved from POWTS discharge into groundwater. Artificial sweeteners—often used as an indicator of municipal wastewater effluent—were found in seven of ten monitoring wells and two water supply wells.

Pete Chase and Jacob Krause, WGNHS, install well casing during a WGRMP-funded experiment designed to improve understanding of virus transport from wastewater to drinking water wells. *Photo: Blake Russo-Nixon*.

Microbial pathogens.

Human enteric virus indicators and pathogenic bacteria indicators have been found in groundwater supply wells in the Madison area (Bradbury et al., 2015). Studies also suggest human enteric viruses from wastewater sources may be present in private and public drinking water wells across the state (Borchardt et al., 2003a, 2003b, 2004, 2007; Bradbury et al. 2013).

Nested piezometers installed for monitoring groundwater levels and sampling for groundwater contaminants near Spring Green. Photo: Blake Russo-Nixon.

Pesticides.

For information on the occurrence of pesticides in Wisconsin's groundwater, see the pesticides section.

GCC Agency Actions

By definition, much is unknown about emerging contaminants, so an important role of the GCC is supporting research studies that further scientific understanding of these substances. In addition to the many studies mentioned above that tested for occurrence of emerging contaminants, other WGRMP-funded projects have explored pathways of contaminant transport. One group of these studies investigated factors that affect the mobility and fate of antibiotics in the subsurface (Gao and Pedersen, 2005 and 2010; Gu and Karthikian, 2005a, 2005b, 2008; Gu et al., 2007; Sibley and Pedersen, 2008; Pedersen et al., 2009). This body of work has helped describe under what conditions specific antibiotic compounds bind to soil, which is important for assessing the risk to groundwater from antibiotics in wastewater sources.

Health effects of emerging contaminants vary and are not always well understood. Some emerging contaminants, including some pesticides and PPCPs, act as endocrine disrupting compounds (EDCs), which adversely affect the behavior of natural hormones in animals and humans. EDCs include both anthropogenic chemicals, such as pesticides and plasticizers, and naturally occurring compounds like steroids and plant-produced estrogens. Scientific studies suggest toxic endpoints varying by compound, with possible health effects including developmental, reproductive, neurologic and immune problems, as well as cancer (NIH, 2010). In many cases, more research is needed.

Periodic groundwater monitoring in areas known to be vulnerable to emerging contaminants is another way in which GCC agencies coordinate efforts to understand emerging contaminants. DATCP's regular statistical survey of agricultural chemicals and targeted monitoring programs in agricultural areas are examples of this. The DNR also regularly reviews groundwater data from near active and closed landfills, mining operations and hazardous waste remediation sites to gather information on potential sources of emerging contaminants.

Future Work

In Wisconsin law, there is an established process for regulated facilitates to review groundwater monitoring data and identify contaminants of emerging concern (WI 160.27). A fundamental component of this process is the long-term groundwater monitoring data itself, so maintenance and expansion of current networks is an ongoing priority for the GCC.

The US Environmental Protection Agency (EPA) also has a process for regularly gathering data on emerging contaminants and assessing potential risks nationwide. The Unregulated Contaminant Monitoring Rule (UCMR) provides for monitoring of unregulated contaminants every five years, in all large (serving > 10,000 people) and a sample of small (serving < 10,000 people) public water systems. The Third

UCMR (UCMR3) monitoring period was completed in 2015. Monitoring for the Fourth UCMR (UCMR4) began during 2018 and focused on select pesticides and several naturally occurring compounds. The Fifth UCMR (UCMR5) will begin in 2023 and will focus on PFAS, with an expanded analyte list and lower detection limits compared to UCMR3. Data collected at Wisconsin public water supply systems during UCMR monitoring along with GCC-supported monitoring and occurrence study results provide valuable information on the occurrence of emerging contaminants in Wisconsin's groundwater resources.

The US EPA also maintains a Contaminant Candidate List (CCL) of physical, chemical, biological and radiological substances that might potentially be found in drinking water. Potential contaminants listed on the CCL are substances not currently subject to federal Safe Drinking Water Act (SDWA) regulation but are known, or anticipated to be present in public water supply systems. The US EPA evaluates occurrence data on these unregulated contaminants and this information assists with identification of potential emerging contaminants in Wisconsin groundwater.

Currently, there are no federal regulatory standards for PFAS associated with any environmental media. As part of a continuing commitment to protect public health, public welfare, and the environment, the DNR periodically updates groundwater quality standards in ch. NR 140, Wis. Adm. Code. In 2018 the DNR requested that DHS review toxicological information available for a number of substances found in Wisconsin groundwater, including two PFAS compounds, PFOA and PFOS. This group of substances DNR asked DHS to review were designated the "Cycle 10" substances. In 2019 the DNR requested that DHS review toxicological information available for another group of substances found in Wisconsin groundwater. This group was designated the "Cycle 11" list of substances and included a number of PFAS compounds.

Based on its review, DHS recommended state groundwater quality standards for many of the substances on the Cycle 10 and 11 lists (see https://www.dhs.wisconsin.gov/water/gws.htm). On February 23, 2022, the DNR Natural Resources Board (NRB) considered approval of proposed revisions to ch. NR 140 to incorporate the DHS Cycle 10 groundwater standard recommendations, including the recommended standards for PFOA and PFOS. The NRB did not approve the proposed NR 140 Cycle 10 groundwater quality standards. The DNR is now evaluating work on substances contained in Cycle 10 and has paused work on rulemaking to incorporate the DHS Cycle 11 groundwater standards recommendations into NR 140.

Further Reading

DNR overview of pharmaceuticals and PCPs in the environment

DNR overview of per- and polyfluoroalkyl substance (PFAS) contamination

Wisconsin Remediation and Redevelopment Database (WRRD)

[DATCP Groundwater Quality Reports]

[NIH factsheet on endocrine disruptors]

[US EPA Third Unregulated Contaminant Monitoring Rule (2012-2016) fact sheets]

[US EPA Third Unregulated Contaminant Monitoring Rule (2012-2016) data summary]

[US EPA Fourth Unregulated Contaminant Monitoring Rule (2017-2021) information]

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